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Oxygen nonstoichiometry, defect equilibria, and thermodynamic characterization of $LaMnO_3$ perovskites with Ca/Sr A-site and Al B-site doping

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ABSTRACT

This work encompasses the thermodynamic characterization of four doped lanthanum manganites, namely $La_{0.6}A_{0.4}Mn_{1-y}Al_yO_3$ (A = Ca, Sr and y = 0, 0.4), all showed to be promising redox materials for the solar thermochemical splitting of H_2O and CO_2 to H_2 and CO. We present oxygen nonstoichiometry measurements in the temperature range T = 1573 K–1773 K and oxygen partial pressure range $p_{O2} = 4.5066 \times 10^{-2}$ bar–9.9×10^{-5} bar. For a given T and p_{O2}, oxygen nonstoichiometry is found to be higher when replacing the divalent dopant Sr in $La_{0.6}Sr_{0.4}MnO_3$ by the divalent Ca but also increases significantly when additionally doping 40 mol-% Al to the Mn-site. $La_{0.6}Ca_{0.4}Mn_{0.6}Al_{0.4}O_3$ revealed the highest mass specific oxygen release, 0.290 mol O_2 per kg metal oxide at T = 1773 K and $p_{O2} = 2.360 \times 10^{-3}$ bar and 0.039 mol kg^{-1} at T = 1573 K and $p_{O2} = 4.5066 \times 10^{-2}$ bar. It is shown that the chemical defect equilibrium of all four perovskites can be accurately described by the two simultaneous redox couples Mn^{4+}/Mn^{3+} and Mn^{3+}/Mn^{2+}. Thermodynamic properties, namely partial molar enthalpy, entropy and Gibbs free energy are consequently extracted from the defect models. Partial molar enthalpy decreases with increasing oxygen nonstoichiometry for the Al-doped perovskites whereas the opposite trend is observed for the others. The enthalpy falls within the range 260–300 kJ mol^{-1} for all the materials. Equilibrium hydrogen yields upon oxidation with H_2O are determined as a function of redox conditions. Although reduction extents of the perovskites are greater compared to CeO_2, oxidation with H_2O and CO_2 is thermodynamically less favorable. This leads to lower mass specific fuel productivity compared to CeO_2 under most conditions relevant for solar thermochemical cycles.

1. Introduction

Nonstoichiometric ceria (CeO_2) is currently considered to be a state-of-the-art redox material for solar-thermochemical splitting of H_2O and CO_2 to H_2 and CO (syngas) because of its rapid oxidation and reduction kinetics and its morphological stability over a range of temperatures and reduction extents [1]. Compared to other metal oxide systems (*e.g.* volatile ZnO [2] and non-volatile ferrites [3,4]), ceria shows relatively low fuel productivity per unit mass of metal oxide [5–7]. It has been shown that reduction extents of ceria can be increased by introducing 4+ valence dopants such as Zr^{4+} [8–12] and Hf^{4+} [8,13] into the ceria lattice. However, thermodynamic calculations for Zr^{4+}-doped ceria [7,12] showed that oxidation with H_2O is less favorable compared to pure ceria. This results in a lower theoretical solar-to-fuel energy conversion efficiency for Zr^{4+}-doped ceria because of larger temperature swings between the redox steps and/or excess oxidant gas [7]. Lower conversion efficiency was also reported for other ceria dopants such as Gd^{3+}, Y^{3+}, Sm^{3+}, Ca^{2+} and Sr^{2+} [6].

Perovskite oxides have recently been proposed as promising alternative reactive intermediates for solar thermochemical H_2O/CO_2 splitting because of potentially increasing the energy conversion efficiency by lowering the reduction temperature or increasing the mass specific fuel yield [14–23]. The two-step solar-thermochemical cycle based on a generic perovskite (ABO_3) is represented by

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$$\frac{1}{\delta_{red}-\delta_{ox}}ABO_{3-\delta_{ox}} \rightarrow \frac{1}{\delta_{red}-\delta_{ox}}ABO_{3-\delta_{red}} + \frac{1}{2}O_2 \quad (1)$$

$$\frac{1}{\delta_{red}-\delta_{ox}}ABO_{3-\delta_{red}} + H_2O \rightarrow \frac{1}{\delta_{red}-\delta_{ox}}ABO_{3-\delta_{ox}} + H_2 \quad (2a)$$

$$\frac{1}{\delta_{red}-\delta_{ox}}ABO_{3-\delta_{red}} + CO_2 \rightarrow \frac{1}{\delta_{red}-\delta_{ox}}ABO_{3-\delta_{ox}} + CO \quad (2b)$$

where Eq. (1) represents the high-temperature endothermic reduction and Eq. (2) the lower temperature exothermic oxidation with H_2O (a) and CO_2 (b). δ_{red} and δ_{ox} represent the oxygen non-stoichiometry after reduction and oxidation, respectively, whereas the difference $\delta_{red} - \delta_{ox}$ is the molar amount of fuel produced per mole of metal oxide. Scheffe et al. [14] considered strontium-doped lanthanum manganites $La_{1-x}Sr_xMnO_3$ (x = 0.30, 0.35, 0.40) and reported reduction extents of $La_{0.6}Sr_{0.4}MnO_3$ to be nearly 6.5 times larger than those of ceria at 1600 K and twice larger at 1800 K, both for $p_{O2} = 10^{-5}$ bar. However, it was shown that their theoretical solar-to-fuel energy conversion efficiency is lower compared to that of ceria because of the thermodynamically less favorable oxidation with CO_2 and H_2O. Based on measurements of Mizusaki et al. [15], Yang et al. [16] concluded higher reduction extents and, consequently, higher fuel yields with increasing x for $La_{1-x}Sr_xMnO_3$ ($0 \leq x \leq 0.5$), while H_2O-to-H_2 conversion rate decreased with increasing x. This led to the conclusion that intermediate doping levels may be optimal for solar-to-fuel energy conversion. McDaniel et al. [17] showed even higher CO and H_2 yields when additionally doping Al to the B-site of $La_{1-x}Sr_xMnO_3$ while maintaining fast oxidation rates with CO_2 and H_2O. Dey et al. [18] showed increasing reduction extents and fuel productivity when replacing the divalent A-site dopant Sr in $La_{1-x}Sr_xMnO_3$ with Ca and obtained best results for x = 0.5. In another recent work [19], they investigated two series of perovskite oxides, $Ln_{0.5}Sr_{0.5}MnO_3$ and $Ln_{0.5}Ca_{0.5}MnO_3$ (Ln = La, Nd, Sm, Gd, Dy, and Y) and concluded highest O_2 release for the manganite with the smallest A-site cation radius (in this case Y). A comparison between $La_xSr_{1-x}MO_3$ (M = Mn, Co, Fe) and $Ba_xSr_{1-x}(Co,Fe)O_3$ [20] showed best results for the Mn-containing perovskites. In a very recent study by Cooper et al. [21], Sr and Ca A-site doped lanthanum-manganites, with and without B-site doping of Al, were examined for redox performance and compared to the state-of-the-art material ceria. $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_3$ and $La_{0.6}Ca_{0.4}Mn_{0.6}Al_{0.4}O_3$ reach four to nine times higher reduction extents compared to ceria in the temperature range T = 1473 K–1673 K, while maintaining fast oxidation kinetics with CO_2. Bork et al. [22] reported that $La_{0.6}Sr_{0.4}Cr_{1-x}Co_xO_3$ with the optimal dopant concentration $x = 0.2$ can split up to 25 times more CO_2 when cycling at T = 1073 K–1473 K compared to ceria or exhibits similar reduction extents (δ = 0.034) at 300 K lower temperatures (1473 K instead of 1773 K). On the other hand, cyclability redox studies by Galvez et al. [23] revealed that the chemical stability of Ca, Sr and Al-doped La–Mn perovskites is detrimentally affected by sintering and by the formation and eventual segregation of a carbonate phase during oxidation by CO_2.

Some of the conclusions drawn for the perovskites discussed above are mainly based on qualitative reduction experiments under an inert flow of low p_{O2} and oxidation under a relatively high flow of CO_2 and/or H_2O in a thermogravimetric analyzer [18–20,22] and/or in an electrically heated furnace coupled to a gas analysis [17,18]. Such experiments with large excess of CO_2 and/or H_2O can result in misleading conclusions, as indicated by various thermodynamic analyses [14,16,21]. In the work of Yang et al. [16], the amount of H_2O needed to oxidize $La_{1-x}Sr_xMnO_3$ ($0 \leq x \leq 0.4$) to a certain δ_{ox}, and hence produce a fixed amount of H_2 in a closed system with variable volume was calculated from thermodynamic data. Similar calculations were performed by Scheffe et al. [14] and Cooper et al. [21], however, there, the initial amount of CO_2 and/or H_2O was fixed and the fuel yield was predicted as a function of oxidation temperature. Such thermodynamic fuel yield calculations allow for an accurate determination of the material's potential to efficiently split CO_2 and/or H_2O.

In this work, we build on the recent work of Cooper et al. [21] and report detailed oxygen nonstoichiometry measurements of $La_{0.6}A_{0.4}Mn_{1-y}Al_yO_3$ (A = Ca, Sr and y = 0, 0.4) over a wide temperature range T = 1573 K–1773 K and oxygen partial pressure range $p_{O2} = 4.5066 \times 10^{-2}$ bar–9.9×10^{-5} bar. The refinement of the nonstoichiometry measurements allows the development of more appropriate defect models to describe the defect chemical equilibria and to extract finer trends in partial molar thermodynamic properties ($\Delta\bar{h}^{\circ}_{O}$, $\Delta\bar{s}^{\circ}_{O}$, $\Delta\bar{g}^{\circ}_{O}$). From such data we determine equilibrium hydrogen yields and evaluate the potential of these lanthanum-manganites to be used as reactive intermediates in solar thermochemical redox cycles.

2. Experimental section

2.1. Sample preparation and characterization

$La_{0.6}Sr_{0.4}MnO_3$ (LSM40), $La_{0.6}Ca_{0.4}MnO_3$ (LCM40), $La_{0.6}Sr_{0.4}Mn_{0.6}Al_{0.4}O_3$ (LSMA) and $La_{0.6}Ca_{0.4}Mn_{0.6}Al_{0.4}O_3$ (LCMA) perovskite powders were synthesized by sol–gel method as described by Scheffe et al. [8]. The corresponding metal nitrates (see Table 1 in electronic supplementary information[1] (ESI)) and anhydrous citric acid (Sigma–Aldrich, catalog nr. 251275) in aqueous solution were used to carry out the synthesis. The ratio of the metal cations to the citric acid was 1:1.5. The aqueous solution was slowly heated up to 573 K to perform the pyrolysis. Afterwards, powders were calcined at 1273 K under air for 5 h. Dense cylindrical pellets were obtained by uniaxially cold-pressing the powder at 5 tons followed by sintering at 1773 K under air atmosphere for 24 h. The approximate dimensions after sintering were 6.4–6.9 mm diameter and 1–2 mm height and the mass of the pellets was ~250 mg (LSM40), ~290 mg (LCM40), ~150 mg (LSMA) and ~270 mg (LCMA). Dopant concentrations were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-OES) and deviated by less than 4% from their nominal composition for LSMA and LCMA. Powder X-ray diffraction (XRD) was performed in the Bragg Brentano geometry using Cu Kα radiation (Philips, PANalytical/X'Pert MPD/DY636, λ = 1.5406 Å, 2Θ = 20–100°, 0.01° s^{-1} scan rate, 45 kV/20 mA output). Scanning electron microscopy (SEM) of the dense pellets was conducted on a TM-1000Microscope (Hitachi, 15 kV accelerating voltage). ICP-OES analysis, XRD patterns and SEM images are shown in ESI.

2.2. Thermal analysis

Oxygen nonstoichiometry was measured using a thermogravimetric analyzer (TGA, Setaram Setsys Evolution). Pellets were suspended to the balance with a custom-made platinum hook to ensure good exposure to the purge gas and eliminate gas diffusion limitations. The p_{O2} of the sweep gas was controlled by mixing Ar (Messer, Argon 4.6) with O_2/Ar mixtures (Messer, 5% O_2 5.0 in Ar 5.0 and 0.1% O_2 5.0 in Ar 5.0). Gases were mixed with electronic mass

[1] Electronic supplementary information (ESI) available: List of metal nitrates used for sample preparation, ICP-OES analysis, XRD patterns, SEM images, detailed derivation of defect model and additional results.